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(71) Applicant and

(72) Inventor: HYON, Man-Sok [KR/KR]; 101-ho,  
Cheongsangseurin Villa, 314-3(16/2), Gwangmyeong-  
dong, Gwangmyeong-si, Gyeonggi-do 423-010 (KR).

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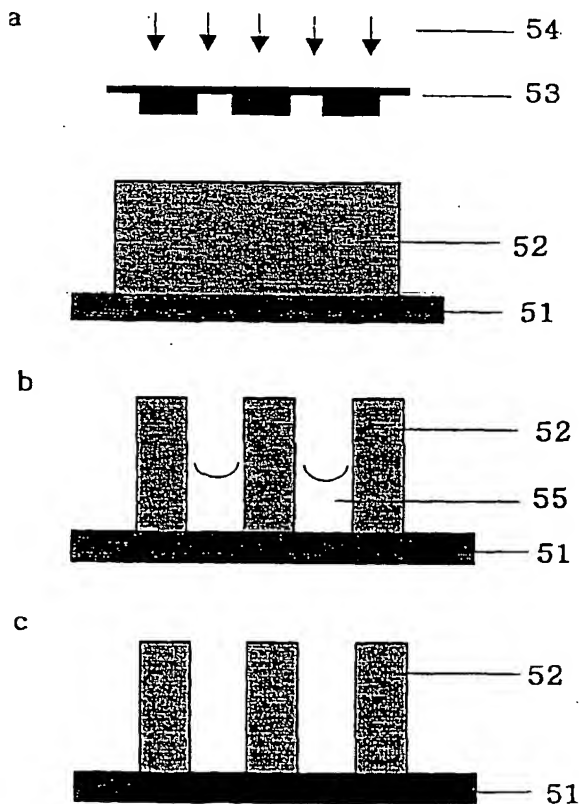
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(54) Title: A METHOD OF FORMING RESIST PATTERNS IN A SEMICONDUCTOR DEVICE AND A SEMICONDUCTOR  
WASHING LIQUID USED IN SAID METHOD



(57) Abstract: This invention relates to a resist patterning method of preventing resist pattern collapse, which is occurred as the minimum pattern size becomes smaller, in photolithography for making semiconductor device and also introduce novel rinse liquid in which fluorocarbon surfactant having hydrophobic group and hydrophilic group is dissolved in deionized water and have low surface tension for preventing resist pattern collapse in wet development method. With this invention, the fine resist pattern can be obtained without resist pattern collapse from conventional wet development method with no additional specific instrument for prevention of resist pattern collapse.

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**A METHOD OF FORMING RESIST PATTERNS IN A SEMICONDUCTOR  
DEVICE AND A SEMICONDUCTOR WASHING LIQUID USED IN SAID  
METHOD**

5

**Technical Field**

The present invention relates to a method of forming a resist pattern of a semiconductor device and semiconductor wafer cleaning liquid used in the method. More particularly, the present invention relates to a method of forming a resist pattern wherein a  
10 resist pattern collapse, which occurs in photolithography for forming the resist pattern onto the a wafer as a minimum resist pattern size (DICD; after Development Inspection Critical Dimension) becomes smaller, can be prevented.

**Background Art**

15 Lithography is a process by which a resist pattern is formed on a wafer by passing light through a mask with a semiconductor circuit patterned thereon so that the pattern can be transferred from the mask to a photoresist. All the layout of the semiconductor device and wiring for use in a semiconductor integrated circuit is formed onto the wafer through the lithographic process.

20 Resist pattern collapse occurs in a development process among the lithographic process, and it is mainly categorized into two types. First, the resist pattern is peeled off from a wafer substrate due to low adhesion therebetween. Second, the resist pattern is curved or broken because of its low rigidity.

Resist pattern collapse in the wet development method occurs in the following  
25 process step. Development process is carried out by the treatment of developing solution and followed by the rinsing with the deionized water and spin drying with high speed rotation of the wafer. In these described steps, the collapse force is driven during spin drying process after the rinse step is finished. The resist pattern is collapsed when it cannot overcome this collapse force.

30 Resist pattern collapse is occurred more easily as the integration of the

semiconductor device is higher. The factors of the resist pattern collapse are the surface tension of the rinse liquid, aspect ratio which is the ratio of pattern height with the pattern width, pattern space and the contact angle between resist pattern and rinse liquid. The relation with these factors is described the following formula. And figure 1 shows  
5 schematic diagram for describing collapse force causing resist pattern collapse

$$\text{Collapse force} = \frac{6\gamma\cos\theta}{D} \left(\frac{H}{W}\right)^2$$

10 where,  $\gamma$  is the surface tension of the rinse liquid,  $\theta$  is the contact angle between the resist pattern and the rinse liquid,  $D$  is the pattern space between the resist patterns,  $H$  is the pattern height and  $W$  is the pattern width. According to the above equation, the collapse force which is the capillary attraction between the resist patterns is proportional to the surface tension of the rinse liquid, aspect ratio and cosine value of the contact angle  
15 between resist pattern and the rinse liquid. And it is an inverse proportional to the pattern space. In the above sentence, the small pattern space means the narrow space between the resist patterns, and small pattern width means that the critical dimension of the resist pattern is small. Therefore, the collapse force becomes more strong as the integration of the semiconductor device gets higher. So pattern collapse is more easily occurred as the  
20 integration of the device gets higher.

Many research has been done to overcome this resist pattern collapse issue in the worldwide. At first, Korean Patent No. 172549 (Korean Patent Application No. 1996-23211) discloses a process for preventing resist pattern collapse by hardening of the resist pattern with the treatment of hot deionized water after washing with the normal  
25 temperature deionized water, and then drying with the spin dry method. This patent is effective to prevent resist pattern collapse which is broken type or bending type. But fine pattern of sub-100nm is too thin to collapse although it is sufficiently strong. So this method has a limit to solve the pattern collapse

Next, Korean Patent Application No. 10-1998-0050982 (Korean Patent Laid-open

Publication No. 2000-0033916) discloses a process technique in which the contact angle between the rinse liquid and resist pattern is made vertical by using vibrator such as ultrasonic generator or electromagnetic wave generator. This method aim to control resist pattern collapse by reducing collapse force by making the contact angle 90 degree.

5        This method assumed that all the surface of the rinse liquid is flat when the wafer is rotated in a high speed of 4000rpm. But all the surface of the rinse liquid cannot be made flat in during such a shot time. Resist pattern collapse can be occurred in some local area in which the surface of the rinse liquid is not flat. It also need to make a new development machine which have a ultrasonic vibrator or elecromagnetic wave generator. Making such  
10    a sophisticated machine is very difficult.

And following two inventions describe the method for preventing resist pattern collapse by lowering surface tension of the rinse liquid.

The Paper, Jpn. J. Appl. Phys. Vol. 32 (1993) pp. 6059, by Toshihiko Tanaka described the method of using new rinse liquid in which tert-butyl alcohol is added to  
15    deionized water to lower the surface tension of rinse liquid. But in this method more than 20% of tert-butyl alcohol is used to make sufficiently low surface tension of the rinse liquid. It cannot be used for the application of semiconductor device because this rinse liquid dissolves the resist pattern so that it changes the critical dimension of the pattern.

The paper, Microelectronic engineering 46 (1999) pp. 129, by Hideo Namatsu  
20    described new process using carbon dioxide with the fact that the surface tension of supercritical fluid is nearly zero. Liquid carbon dioxide is ejected on the wafer at the temperature of below 10°C , and then the temperature is elevated to above 35°C and pressure is optimized at high pressure of around 7.5Mpa. In this hard condition the carbon dioxide becomes supercritical fluid, which is the condition of gas having high density or  
25    liquid state being capable of diffusion. There is no boundary between gas state and liquid state in supercritical condition.

But this method use liquid carbon dioxide of highly expensive and should develop new machine which can control the temperature from 10°C to 35°C and make high pressure of 7.5Mpa. Moreover, this method should eject carbon dioxide of supercritical

fluid at low speed of 1 liter per minute. It takes much time to process one wafer so that it produces low throughput. It is strong demerit for the mass production of semiconductor device and questionable for the real application.

5    **Disclosure of Invention**

        This invention aims to provide new resist patterning technology which is preventing resist pattern collapse at the micro patterns.

        And, this invention aims to provide resist patterning technology without additional new machine for the prevention of resist pattern collapse, which use conventional  
10   development machine.

        And this invention aims to provide additives whose solution in water have low surface tension and does not dissolve resist pattern.

        And this invention aims to provide new rinse liquid which can prevent resist pattern collapse.

15

**Brief Description of Drawings**

        FIG. 1 is a schematic view showing width and height of a resist pattern for explaining force used for causing the resist pattern to collapse.

        FIG. 2 is a sectional view illustrating a conventional process for forming a fine  
20   resist pattern.

        FIG. 3 is a graph showing relationship between a surface tension and a concentration of fluorocarbon surfactant having hydrophilic group and hydrophobic group according to the present invention.

        FIG. 4 is a sectional view illustrating a principle that a surface tension of water  
25   solution with fluorocarbon surfactant having hydrophilic group and hydrophobic group added therein is lowered according to the present invention.

        FIG. 5 is a sectional view illustrating a process for forming a resist pattern according to a first embodiment of the present invention.

        FIG. 6 is a sectional view illustrating a process for forming a resist pattern

according to a second embodiment of the present invention.

### **Best Mode for Carrying Out the Invention**

The method to achieve these goals for the patterning of resist pattern without resist  
 5 pattern collapse is using novel rinse liquid in which the fluorocarbon surfactant having hydrophobic group and hydrophilic group is dissolved in deionized water. This solution is called "SPPC", solution for preventing resist pattern collapse. It is used for the production of semiconductor devices which contain memory semiconductor device, logic device and semiconductor for the LCD products.

10 The fluorocarbon surfactant having both characteristics of hydrophilic group and hydrophobic group has chemical formula of  $C_aH_bF_cO_dS_eN_f$ , where "a" is an integer having range from 1 to 20, "b" is an integer having range from 0 to 30, "c" is an integer having range from 1 to 30, "d" is an integer having range from 1 to 8, "e" is an integer having range from 0 to 2, and "f" is an integer having range from 0 to 2.

15 The hydrophobic group is hydrocarbon or fluorocarbon and the hydrophilic group is carboxylic acid or sulfonic acid.

Here is examples for the fluorocarbon surfactant in which there are both functional group of hydrophobic group and hydrophilic group ;

20 Difluoroacetic acid ( $C_2H_2F_2O_2$ ), 2,2,3,3-Tetrafluoropropionic acid ( $C_3H_2F_4O_2$ ), 3,3,3-Trifluoropropionic acid ( $C_3H_3F_3O_2$ ), Heptafluorobutyric acid ( $C_4HF_7O_2$ ), Tetrafluorosuccinic acid ( $C_4H_2F_4O_4$ ), 3,3,3-Trifluoro-2-(trifluoromethyl) propionic acid ( $C_4H_2F_6O_2$ ), 2-(Trifluoromethyl)acrylic acid ( $C_4H_3F_3O_2$ ), Nonafluoropentanoic acid ( $C_5HF_9O_2$ ), Hexafluoroglutaric acid ( $C_5H_2F_6O_4$ ), 4,4,4-Trifluoro-3-methyl-2-butenic acid ( $C_5H_5F_3O_2$ ), 2,2,3,3,4,4,5,5,6,6,7,7-Dodecafluoroheptanoic acid ( $C_7H_2F_{12}O_2$ ),  
 25 Trifluorobenzoic acid ( $C_7H_3F_3O_2$ ), Difluorobenzoic acid ( $C_7H_4F_2O_2$ ), Fluorobenzoic acid ( $C_7H_5FO_2$ ), Pentadecafluorooctanoic acid ( $C_8HF_{15}O_2$ ), Tetrafluoroisophthalic acid ( $C_8H_2F_4O_4$ ), Tetrafluorophthalic acid ( $C_8H_2F_4O_4$ ), Tetrafluoroterephthalic acid ( $C_8H_2F_4O_4$ ), Perfluorosuberic acid ( $C_8H_2F_{14}O_4$ ), 2,3,4,5,6-Pentafluorophenylacetic acid ( $C_8H_3F_5O_2$ ), 2,3,4,5,6-Pentafluorophenoxyacetic acid ( $C_8H_3F_5O_3$ ), Perfluoroadipic

acid( $C_6H_2F_8O_4$ ), Pentafluorobenzoic acid( $C_7HF_7$ ), Tridecafluoroheptanoic acid( $C_7HF_{13}O_2$ ),  
 2,3,4,5-Tetrafluorobenzoic acid( $C_7H_2F_4O_2$ ), 2,3,4,6-Tetrafluorobenzoic acid( $C_7H_2F_4O_2$ ),  
 Fluoro-(trifluoromethyl)benzoic acid( $C_8H_4F_4O_2$ ), 2,3,6-trifluorophenylacetic  
 acid( $C_8H_6F_2O_2$ ), 4-(difluoromethoxy)benzoic acid( $C_8H_6F_2O_3$ ), Heptadecafluorononaic  
 5 acid( $C_9HF_{17}O_2$ ), 2,3,4,5,6-Pentafluorocinnamic acid( $C_9H_3F_5O_2$ ), bis(trifluoromethyl)  
 benzoic acid( $C_9H_4F_6O_2$ ), 2,3,4-Trifluorocinnamic acid( $C_9H_5F_3O_2$ ), Difluorocinnamic  
 acid( $C_9H_6F_2O_2$ ), Fluorocinnamic acid( $C_9H_7FO_2$ ), (Trifluoro) acetic acid( $C_9H_7F_3O_2$ ), 4-  
 (trifluoromethyl)mandelic acid( $C_9H_7F_3O_2$ ), Nonadecafluorodecanoic acid( $C_{10}HF_{19}O_2$ ),  
 Perfluorosebacic acid( $C_{10}H_2F_{16}O_4$ ), Bis(trifluoromethyl)phenylacetic acid( $C_{10}H_6F_6O_2$ ), 2-  
 10 (trifluoromethyl)cinnamic acid( $C_{10}H_7F_3O_2$ ), 4-(3,5-difluorophenyl)-4-oxobutyric  
 acid( $C_{10}H_8F_2O_3$ ), 4-(trifluoromethyl)hydrocinnamic acid( $C_{10}H_9F_3O_2$ ),  
 Perfluoroundecanoic acid( $C_{11}HF_{21}O_2$ ), Bis(trifluoromethyl)hydrocinnamic  
 acid( $C_{11}H_8F_6O_2$ ), Perfluorododecanoic acid( $C_{12}HF_{23}O_2$ ), Perfluorotetradecanoic  
 acid( $C_{14}HF_{27}O_2$ ), Perfluorotridecanoic acid( $C_{13}HF_{25}O_2$ ), Bis(benzoic acid) ( $C_{17}H_{10}F_6O_4$ )

15

One example in which the resist pattern is formed for the making semiconductor device using the SPPC, solution for preventing resist pattern collapse, is described in detail. The first step is coating wafer with photoresist and baking the wafer. The second step is exposing the photoresist with light using reticle and baking the wafer. The third step is  
 20 developing the photoresist with developing solution. The fourth step is washing the photoresist with the SPPC which is the solution for preventing resist pattern collapse and dissolving fluorocarbon surfactant having hydrophobic group and hydrophilic group in deionized water. The fifth step is spin-drying the wafer and finish forming the resist pattern on the wafer. In the previous example, the fourth step can be divided into two sub steps,  
 25 in which the first sub step is washing the wafer with normal deionized water for the removal of the polymer residue and developing solution. The second sub step is spraying the SPPC before spin drying. This provides advantage for low cost because the SPPC is more expensive than the deionized water and use more little SPPC for the process

The followings are detail explanations with the attached drawing for the above



example. The conventional process is explained with figure 2a, 2b, and 2c for comparison with this invention.

In the figure 2, the symbol 21 means wafer substrate, symbol 22 means photoresist, symbol 23 means mask, symbol 24 means light source and symbol 25 means developing solution.

As shown in figure 2a, photoresist(22) is coated on the wafer substrate(21) and then soft bake is carried out. After that light(24) is exposed through the mask(23). Post exposure bake is carried out. And resist pattern shown in figure 2b is formed by the treatment of developing solution. The wafer is washed with deionized water and then dried with high speed rotation of the wafer. As shown in figure 2c, resist pattern collapse can be brought out when the spin dry step begins after washing with deionized water.

Now the invention process is explained in detail. The invention aims for the patterning of resist pattern without resist pattern collapse using novel rinse liquid which contains the fluorocarbon surfactant having hydrophobic group and hydrophilic group in deionized water so that it have low surface tension and does not dissolve the resist pattern

The solution, which contains even small amount of the fluorocarbon surfactant having hydrophobic group and hydrophilic group in deionized water, has low surface tension and does not dissolve the resist pattern. When this solution is used for the rinse liquid, the resist pattern collapse can be prevented.

The following data demonstrate the low surface tension of the solution containing fluorocarbon surfactant having hydrophobic group and hydrophilic group in deionized water and explains the principle of lowering surface tension.

Table 1 shows the surface tension of the solution containing fluorocarbon surfactant having hydrophobic group and hydrophilic group. It was reported at the paper, Journal of Physical Chemistry, Vol. 76, No. 6,(1972) pp. 909, by Kozo Shinoda as the title of "The physicochemical properties of aqueous solutions of fluorinated surfactants"

【Table 1】 The surface tension of the solution containing fluorocarbon surfactant having hydrophobic group and hydrophilic group.

| compound  | Minima of Surface tension,<br>dynes/cm | Cross sectional area,<br>2/molecule |
|---|--|-------------------------------------|
| n-C <sub>7</sub> F <sub>15</sub> SO <sub>3</sub> Na   | 37.3                                   | 52.5                                |
| n-C <sub>8</sub> F <sub>17</sub> SO <sub>3</sub> Li   | 29.8                                   | 52.2                                |
| n-C <sub>8</sub> F <sub>17</sub> SO <sub>3</sub> Na   | 40.5                                   | 52.5                                |
| n-C <sub>8</sub> F <sub>17</sub> SO <sub>3</sub> K  | 34.5                                   | 45.1                                |
| n-C <sub>8</sub> F <sub>17</sub> SO <sub>3</sub> NH <sub>4</sub>                                  | 27.8                                   | 41.0                                |
| n-C <sub>8</sub> F <sub>17</sub> SO <sub>3</sub> NH <sub>3</sub> C <sub>2</sub> H <sub>4</sub> OH | 21.5                                   | 42.5                                |
| n-C <sub>9</sub> F <sub>19</sub> SO <sub>3</sub> ·1/2Mg·2H <sub>2</sub> O                         | 22.0                                   | 45.2                                |
| n-C <sub>7</sub> F <sub>15</sub> COONa  | 24.6                                   | 42.0                                |
| (CF <sub>3</sub> ) <sub>2</sub> CF(CF <sub>2</sub> ) <sub>4</sub> COONa                           | 20.2                                   | 43.5                                |
| n-C <sub>7</sub> F <sub>15</sub> COOK   | 20.6                                   | 43.0                                |
| (CF <sub>3</sub> ) <sub>2</sub> CF(CF <sub>2</sub> ) <sub>4</sub> COOK                            | 19.5                                   | 47.5                                |
| n-C <sub>7</sub> F <sub>15</sub> COOH   | 15.2                                   | 41.5                                |
| (CF <sub>3</sub> ) <sub>2</sub> CF(CF <sub>2</sub> ) <sub>4</sub> COOH                            | ~15.2                                  | 48.0                                |
| (CF <sub>3</sub> ) <sub>2</sub> CF(CF <sub>2</sub> ) <sub>4</sub> CH=CCHCH <sub>2</sub> COOK*     | 19.4                                   | ....                                |

\* In 0.02N aqueous KOH solution

5

As shown in table 1, the surface tension of pentadecafluorooctanoic acid, n-C<sub>7</sub>F<sub>15</sub>COOH, is 15.2 dyne/cm. It is quite small value comparing with the fact that the surface tension of water is 72 dyne/cm, that of bromobenzene is 35.75 dyne/cm, and that of n-octanol is 27.53 dyne/cm.

10

The surface tension is related to the interaction between molecules so that the surface tension of water is large because it have hydrogen bond between molecules and that of surfactant is small because there is little interaction between hydrophobic groups.

The solution containing fluorocarbon surfactant having hydrophilic group and

hydrophobic group has low surface tension because the hydrophilic group of the compound in the water surface points downward to water and the hydrophobic group of the compound in the water surface points upward to air as shown in figure 4. The symbol 41 is wafer substrate, symbol 42 is solution for preventing resist pattern collapse, symbol 43 is fluorocarbon surfactant having both hydrophobic group and hydrophilic group, symbol 44 is photoresist.

As the number of carbon in the fluorocarbon surfactant is larger, the number of molecules whose hydrophobic group toward to air is larger and the degree of this orientation is larger, so the surface tension of the compound becomes lower.

Figure 3 shows the surface tension vs. the concentration of the fluorocarbon surfactant. This shows the small concentration of the fluorocarbon surfactant can sufficiently lower the surface tension of the solution, and this fact is important for the practical use because the fluorocarbon surfactant costs a lot.

The x axis is the concentration of the solution and the y axis is the surface tension of the solution. The solution of pentadecafluorooctanoic acid has small surface tension of 15 dyne/cm at the low concentration of 0.01M. This value is significantly low compared with normal water having surface tension of 72 dyne/cm.

According to table 1, the salt form of the fluorocarbon surfactant has also low surface tension. So the salt form of fluorocarbon surfactant with LiOH, NaOH, or KOH can be used for the making novel rinse liquid.

The salt compound of this fluorocarbon surfactant can be made with ammoniumhydroxide, Tetramethyl ammoniumhydroxide, Tetrabutyl ammoniumhydroxide, Tetrapropyl ammoniumhydroxide, ethanol ammoniumhydroxide, diethanol ammoniumhydroxide, triethanol ammoniumhydroxide.

The rinse liquid can be made by the salt compound of fluorocarbon surfactant or hydrocarbon compound having hydrophobic group and hydrophilic group with Li, Na, or  $\text{NH}_a\text{R}^+_b\text{OH}^-$  where a is an integer ranging from 0 to 4, b is an integer ranging from 0 to 4, R is  $\text{CH}_3$ ,  $\text{C}_4\text{H}_9$ ,  $\text{C}_3\text{H}_7$ ,  $\text{C}_2\text{H}_4\text{OH}$ , or moiety having alkyl or alcohol or ether whose number of carbon is ranging from 1 to 20.

With these properties, this solution is used for the prevention of resist pattern collapse in semiconductor device fabrication.

The new resist process is explained with in detail using the solution for preventing resist pattern collapse as rinse liquid with figure 5 and figure 6.

5        Figure 5a, figure 5b, and figure 5c show the resist patterning method according to the example 1. The symbol 51 is wafer substrate, symbol 52 is photoresist, symbol 53 is mask, symbol 54 is light source and symbol 55 is the solution for preventing resist pattern collapse.

10        As shown in figure 5a, photoresist(52) is coated at the thickness of 4000 Å on the wafer substrate(51) and then soft bake is carried out for 90seconds at the temperature of 100°C. After that light(54) of 248nm wavelength is exposed through the mask(53). Post exposure bake is carried out for 90seconds at the temperature of 100°C. . Development was carried out with treatment of 2.38% TMAH developing solution, and washing with 0.02M pentadecafluorooctanoic acid solution(55) as shown in figure 5b. And the wafer is dried  
15        with high speed rotation of 4000rpm. As shown in figure 5c, resist pattern was formed without resist pattern collapse.

20        The developing solution of TMAH, tetramethylammonium hydroxide, can make salt form by the reaction with acid solution of preventing resist pattern collapse, so the drain can be separated with the conventional drain of developing solution. The mixing of SPPC with developing solution can be avoided by the use of another drain for SPPC. The conventional machine for development can be easily modified to specific machine for the use of spin dry process using SPPC which have another drain, which have different drain with that of developing solution.

25        Figure 6a, figure 6b, figure 6c and figure 6d show the resist patterning method according to the example 2. The symbol 61 is wafer substrate, symbol 62 is photoresist, symbol 63 is mask, symbol 64 is light source and symbol 65 is the deionized water, and symbol 66 is SPPC, solution for preventing resist pattern collapse.

As shown in figure 6a, photoresist(62) is coated at the thickness of 4000 Å on the wafer substrate(61) and then soft bake is carried out for 90seconds at the temperature of

100°C. After that light(64) of 248nm wavelength is exposed through the mask(63). Post exposure bake is carried out for 90seconds at the temperature of 100°C. The developent was carried out with 2.38% TMAH solution, and the washing of the wafer with deionized water(65) was carried out with the rotation of the wafer at the low speed of 500rpm for 5 seconds as shown in drawing 6b. And then rinsing with 0.05M pentadecafluorooctanoic acid solution(66) is performed as shown in drawing 6c. After drying with high speed rotation of 4000rpm, resist pattern was formed without resist pattern collapse as shown in drawing 6d,

The volume of used SPFC in the example 2 is smaller than that of example 1 because SPFC is used after washing with deionized water in example 2. So the example 2 is more cost effective compared with the example 1.

The solution containing fluorocarbon surfactant having hydrophobic group and hydrophilic group is used for the rinse liquid because it serves low surface tension. With this concept, the solution of hydrocarbon containing hydrophilic group and hydrophobic group can also be used for the rinse liquid if its hydrophobic group is sufficiently good so that the molecule of looking upward is high in the surface and then the solution has sufficiently low surface tension.

The chemical formula of hydrocarbon surfactant is  $C_aH_bO_cS_dN_eP_f$ , where a is integer ranging from 1 to 30, b is integer ranging from 1 to 60, c is integer ranging from 1 to 10, d is integer ranging from 0 to 2, e is integer ranging from 0 to 2, f is integer ranging from 0 to 2. The hydrophobic group is saturated hydrocarbon or unsaturated hydrocarbon, and the hydrophilic group is carboxylic acid or sulfonic acid or sulfuric acid or alcohol. The resist patterning process use novel rinse liquid in which there are one or more hydrocarbon surfactant like following; dodecyl sulfuric acid  $C_{12}H_{25}SO_4H$ , dodecyl monooxyethylene sulfuric acid  $C_{12}H_{25}(OCH_2CH_2)SO_4H$ , dodecyl dioxyethylene sulfuric acid  $C_{12}H_{25}(OCH_2CH_2)_2SO_4H$ , dodecyl trioxyethylene sulfuric acid  $C_{12}H_{25}(OCH_2CH_2)_3SO_4H$ , dodecyl hexaoxyethylene sulfuric acid,  $C_{12}H_{25}(OCH_2CH_2)_6SO_4H$ .

The invention was explained with invention example, but the range of this

invention should not be limited by this example and should be interpreted with the claims of invention.

#### **Industrial Applicability**

5       According to this invention, micro pattern can be formed without resist pattern collapse with usage of the solution for preventing resist pattern collapse as rinse liquid.

Additional investment for new process or new machine such as using dry development, bi-layer process or tri-layer process is not necessary because it use conventional wet development method. So it makes more cost-effective production.

10

### CLAIMS

1. A method of forming a resist pattern of a semiconductor device, comprising the steps of:

5       coating a photoresist onto a wafer and baking the wafer;  
      exposing the wafer using a mask and baking the wafer;  
      developing the exposed photoresist with developer so that a photoresist pattern is formed;  
      rinsing the wafer with deionized water to which a fluorocarbon surfactant  
10       containing hydrophobic group and hydrophilic group is added;  
      completing the pattern of the photoresist pattern by rotating the wafer at a high speed so that the deionized water to which fluorocarbon surfactant having hydrophobic group and hydrophilic group is added is evaporated.
- 15 2. A method of forming a resist pattern of a semiconductor device, comprising the steps of:

      coating a photoresist onto a wafer and baking the wafer;  
      exposing the wafer using a mask and baking the wafer;  
20       developing the exposed photoresist with developer so that a photoresist pattern is formed;  
      cleaning the wafer with deionized water and       evaporating a portion of the deionized water by rotating the wafer at a low speed;  
      rinsing the wafer with the deionized water to which fluorocarbon surfactant having  
25       hydrophobic group and hydrophilic group is added;  
      completing the photoresist pattern by rotating the wafer at a high speed so that the deionized water to which fluorocarbon surfactant having hydrophobic group and hydrophilic group is added is evaporated.

3. The method as claimed in claim 1 or 2, wherein the resist patterning process use novel rinse liquid in which there are fluorocarbon surfactants having the chemical formula of  $C_aH_bF_cO_dS_eN_f$ , where a is an integer ranging from 1 to 20, b is an integer ranging from 0 to 30, c is an integer ranging from 1 to 30, d is an integer ranging from 1 to 8, e is an integer ranging from 0 to 2, f is an integer ranging from 0 to 2.
4. The method as claimed in claim 1 or 2, wherein the resist patterning process use novel rinse liquid in which there are fluorocarbon surfactants or hydrocarbon surfactants having hydrophobic group and hydrophilic group. The hydrophobic group is hydrocarbon or fluorocarbon and the hydrophilic group is carboxylic acid or sulfonic acid or sulfuric acid or alcohol.
5. The method as claimed in claim 1 or 2, wherein the fluorocarbon surfactant is a material selected from the group consisting of:
- 15 Difluoroacetic acid ( $C_2H_2F_2O_2$ ), 2,2,3,3-Tetrafluoropropionic acid ( $C_3H_2F_4O_2$ ), 3,3,3-Trifluoropropionic acid ( $C_3H_3F_3O_2$ ), Heptafluorobutyric acid ( $C_4HF_7O_2$ ), Tetrafluorosuccinic acid ( $C_4H_2F_4O_4$ ), 3,3,3-Trifluoro-2-(trifluoromethyl) propionic acid ( $C_4H_2F_6O_2$ ), 2-(Trifluoromethyl)acrylic acid ( $C_4H_3F_3O_2$ ), Nonafluoropentanoic acid ( $C_5HF_9O_2$ ), Hexafluoroglutaric acid ( $C_5H_2F_6O_4$ ), 4,4,4-Trifluoro-3-methyl-2-butenic acid ( $C_5H_5F_3O_2$ ), 2,2,3,3,4,4,5,5,6,6,7,7-Dodecafluoroheptanoic acid ( $C_7H_2F_{12}O_2$ ), Trifluorobenzoic acid ( $C_7H_3F_3O_2$ ), Difluorobenzoic acid ( $C_7H_4F_2O_2$ ), Fluorobenzoic acid ( $C_7H_5FO_2$ ), Pentadecafluorooctanoic acid ( $C_8HF_{15}O_2$ ), Tetrafluoroisophthalic acid ( $C_8H_2F_4O_4$ ), Tetrafluorophthalic acid ( $C_8H_2F_4O_4$ ), Tetrafluoroterephthalic acid ( $C_8H_2F_4O_4$ ), Perfluorosuberic acid ( $C_8H_2F_{14}O_4$ ), 2,3,4,5,6-Pentafluorophenylacetic acid ( $C_8H_3F_5O_2$ ), 2,3,4,5,6-Pentafluorophenoxyacetic acid ( $C_8H_3F_5O_3$ ), Perfluoroadipic acid ( $C_6H_2F_8O_4$ ), Pentafluorobenzoic acid ( $C_7HF_7$ ), Tridecafluoroheptanoic acid ( $C_7HF_{13}O_2$ ), 2,3,4,5-Tetrafluorobenzoic acid ( $C_7H_2F_4O_2$ ), 2,3,4,6-Tetrafluorobenzoic acid ( $C_7H_2F_4O_2$ ), Fluoro-(trifluoromethyl)benzoic acid ( $C_8H_4F_4O_2$ ), 2,3,6-trifluorophenylacetic acid ( $C_8H_6F_2O_2$ ), 4-(difluoromethoxy)benzoic acid ( $C_8H_6F_2O_3$ ), Heptadecafluorononaic



acid( $C_9H_7F_3O_2$ ), 2,3,4,5,6-Pentafluorocinnamic acid( $C_9H_3F_5O_2$ ), bis(trifluoromethyl) benzoic acid( $C_9H_4F_6O_2$ ), 2,3,4-Trifluorocinnamic acid( $C_9H_5F_3O_2$ ), Difluorocinnamic acid( $C_9H_6F_2O_2$ ), Fluorocinnamic acid( $C_9H_7FO_2$ ), (Trifluoro) acetic acid( $C_9H_7F_3O_2$ ), 4-(trifluoromethyl)mandelic acid( $C_9H_7F_3O_2$ ), Nonadecafluorodecanoic acid( $C_{10}HF_{19}O_2$ ),  
 5 Perfluorosebacic acid( $C_{10}H_2F_{16}O_4$ ), Bis(trifluoromethyl)phenylacetic acid( $C_{10}H_6F_6O_2$ ), 2-(trifluoromethyl)cinnamic acid( $C_{10}H_7F_3O_2$ ), 4-(3,5-difluorophenyl)-4-oxobutyric acid( $C_{10}H_8F_2O_3$ ), 4-(trifluoromethyl)hydrocinnamic acid( $C_{10}H_9F_3O_2$ ), Perfluoroundecanoic acid( $C_{11}HF_{21}O_2$ ), Bis(trifluoromethyl)hydrocinnamic acid( $C_{11}H_8F_6O_2$ ), Perfluorododecanoic acid( $C_{12}HF_{23}O_2$ ), Perfluorotetradecanoic  
 10 acid( $C_{14}HF_{27}O_2$ ), Perfluorotridecanoic acid( $C_{13}HF_{25}O_2$ ), Bis(benzoic acid) ( $C_{17}H_{10}F_6O_4$ ).

6. In the claim 1 or claim 2, the resist patterning process use 365nm, 248nm, 193nm, 157nm, EUV(13nm), X-ray or e-beam or ion as the light source.

15 7. In claim 2, the resist process in which the low spin speed have the range from 10 to 1000rpm and the high spin speed have range from 2000 to 4000rpm.

8. A method of forming a resist pattern of a semiconductor device, comprising the steps of:

20 coating a photoresist onto a wafer and baking the wafer;  
 exposing the wafer using a mask and baking the wafer;  
 developing the exposed photoresist with developer so that a photoresist pattern is formed;  
 rinsing the wafer with deionized water to which hydrocarbon compound  
 25 containing hydrophobic group and hydrophilic group is added;  
 completing the pattern of the photoresist pattern by rotating the wafer at a high speed so that the deionized water to which hydrocarbon compound having hydrophobic group and hydrophilic group is added is evaporated.

9. A method of forming a resist pattern of a semiconductor device, comprising the steps of:

coating a photoresist onto a wafer and baking the wafer;

exposing the wafer using a mask and baking the wafer;

5 developing the exposed photoresist with developer so that a photoresist pattern is formed;

cleaning the wafer with deionized water and evaporating a portion of the deionized water by rotating the wafer at a low speed;

10 rinsing the wafer with the deionized water to which hydrocarbon compound having hydrophobic group and hydrophilic group is added;

completing the photoresist pattern by rotating the wafer at a high speed so that the deionized water to which hydrocarbon compound having hydrophobic group and hydrophilic group is added is evaporated.

15 10. In the claim 8 or claim 9, the resist patterning process use novel rinse liquid in which there are hydrocarbon surfactants having the chemical formula of  $C_aH_bO_cS_dN_eP_f$ , where a is an integer ranging from 1 to 30, b is an integer ranging from 1 to 60, c is an integer ranging from 1 to 10, d is an integer ranging from 0 to 2, e is an integer ranging from 0 to 2, f is an integer ranging from 0 to 2. If the compound is alcohol, a is an integer ranging from 5 to 30, b is an integer ranging from 1 to 60, c is an integer ranging from 1 to 10, d is an integer ranging from 0 to 2, e is an integer ranging from 0 to 2, f is an integer ranging from 0 to 2.

25 11. In the claim 8 or claim 9, the resist patterning process use novel rinse liquid in which there is hydrocarbon surfactants having hydrophobic group and hydrophilic group. The hydrophobic group is saturated hydrocarbon or unsaturated hydrocarbon and the hydrophilic group is carboxylic acid or sulfonic acid or sulfuric acid or alcohol.

12. In the claim 8 or claim 9, the resist patterning process use novel rinse liquid in

which there are one or more hydrocarbon surfactant like following;

dodecyl sulfuric acid  $C_{12}H_{25}SO_4H$ , dodecyl monooxyethylene sulfuric acid  $C_{12}H_{25}(OCH_2CH_2)SO_4H$ , dodecyl dioxyethylene sulfuric acid  $C_{12}H_{25}(OCH_2CH_2)_2SO_4H$ , dodecyl trioxyethylene sulfuric acid  $C_{12}H_{25}(OCH_2CH_2)_3SO_4H$ ,  
 5 dodecyl hexaoxyethylene sulfuric acid,  $C_{12}H_{25}(OCH_2CH_2)_6SO_4H$ .

13. The rinse liquid in which the fluorocarbon surfactant having hydrophobic group and hydrophilic group is dissolved in deionized water. The chemical formula of the fluorocarbon surfactant is  $C_aH_bF_cO_dS_eN_f$ , where a is an integer ranging from 1 to 20, b is an integer ranging from 0 to 30, and c is an integer 1 to 30, and d is an integer ranging from 1  
 10 to 8, and e is an integer ranging from 0 to 2, f is an integer ranging from 0 to 2.

14. In claim 13, the rinse liquid is made by fluorocarbon surfactant whose the hydrophobic group is hydrocarbon or fluorocarbon and the hydrophilic group is carboxylic  
 15 acid, sulfonic acid or alcohol.

15. In claim 13, the rinse liquid is made by the following chemical.

Difluoroacetic acid ( $C_2H_2F_2O_2$ ), 2,2,3,3-Tetrafluoropropionic acid ( $C_3H_2F_4O_2$ ), 3,3,3-Trifluoropropionic acid ( $C_3H_3F_3O_2$ ), Heptafluorobutyric acid ( $C_4HF_7O_2$ ),  
 20 Tetrafluorosuccinic acid ( $C_4H_2F_4O_4$ ), 3,3,3-Trifluoro-2-(trifluoromethyl) propionic acid ( $C_4H_2F_6O_2$ ), 2-(Trifluoromethyl)acrylic acid ( $C_4H_3F_3O_2$ ), Nonafluoropentanoic acid ( $C_5HF_9O_2$ ), Hexafluoroglutaric acid ( $C_5H_2F_6O_4$ ), 4,4,4-Trifluoro-3-methyl-2-butenic acid ( $C_5H_5F_3O_2$ ), 2,2,3,3,4,4,5,5,6,6,7,7-Dodecafluoroheptanoic acid ( $C_7H_2F_{12}O_2$ ), Trifluorobenzoic acid ( $C_7H_3F_3O_2$ ), Difluorobenzoic acid ( $C_7H_4F_2O_2$ ), Fluorobenzoic  
 25 acid ( $C_7H_5FO_2$ ), Pentadecafluorooctanoic acid ( $C_8HF_{15}O_2$ ), Tetrafluoroisophthalic acid ( $C_8H_2F_4O_4$ ), Tetrafluorophthalic acid ( $C_8H_2F_4O_4$ ), Tetrafluoroterephthalic acid ( $C_8H_2F_4O_4$ ), Perfluorosuberic acid ( $C_8H_2F_{14}O_4$ ), 2,3,4,5,6-Pentafluorophenylacetic acid ( $C_8H_3F_5O_2$ ), 2,3,4,5,6-Pentafluorophenoxyacetic acid ( $C_8H_3F_5O_3$ ), Perfluoroadipic acid ( $C_6H_2F_8O_4$ ), Pentafluorobenzoic acid ( $C_7HF_7$ ), Tridecafluoroheptanoic acid ( $C_7HF_{13}O_2$ ),

2,3,4,5-Tetrafluorobenzoic acid( $C_7H_2F_4O_2$ ), 2,3,4,6-Tetrafluorobenzoic acid( $C_7H_2F_4O_2$ ),  
 Fluoro-(trifluoromethyl)benzoic acid( $C_8H_4F_4O_2$ ), 2,3,6-trifluorophenylacetic  
 acid( $C_8H_6F_2O_2$ ), 4-(difluoromethoxy)benzoic acid( $C_8H_6F_2O_3$ ), Heptadecafluorononaic  
 acid( $C_9HF_{17}O_2$ ), 2,3,4,5,6-Pentafluorocinnamic acid( $C_9H_3F_5O_2$ ), bis(trifluoromethyl)  
 5 benzoic acid( $C_9H_4F_6O_2$ ), 2,3,4-Trifluorocinnamic acid( $C_9H_5F_3O_2$ ), Difluorocinnamic  
 acid( $C_9H_6F_2O_2$ ), Fluorocinnamic acid( $C_9H_7FO_2$ ), (Trifluoro) acetic acid( $C_9H_7F_3O_2$ ), 4-  
 (trifluoromethyl)mandelic acid( $C_9H_7F_3O_2$ ), Nonadecafluorodecanoic acid( $C_{10}HF_{19}O_2$ ),  
 Perfluorosebacic acid( $C_{10}H_2F_{16}O_4$ ), Bis(trifluoromethyl)phenylacetic acid( $C_{10}H_6F_6O_2$ ), 2-  
 (trifluoromethyl)cinnamic acid( $C_{10}H_7F_3O_2$ ), 4-(3,5-difluorophenyl)-4-oxobutyric  
 10 acid( $C_{10}H_8F_2O_3$ ), 4-(trifluoromethyl)hydrocinnamic acid( $C_{10}H_9F_3O_2$ ), Perfluoroundecanoic  
 acid( $C_{11}HF_{21}O_2$ ), Bis(trifluoromethyl)hydrocinnamic acid( $C_{11}H_8F_6O_2$ ),  
 Perfluorododecanoic acid( $C_{12}HF_{23}O_2$ ), Perfluorotetradecanoic acid( $C_{14}HF_{27}O_2$ ),  
 Perfluorotridecanoic acid( $C_{13}HF_{25}O_2$ ), Bis(benzoic acid) ( $C_{17}H_{10}F_6O_4$ ).

15 16. In claim 13 or claim 14 or claim 15, the concentration of the fluorocarbon  
 surfactant having hydrophobic group and hydrophilic group is ranging from 0.001M to  
 0.1M.

17. In claim 16, the concentration of the fluorocarbon surfactant having hydrophobic  
 20 group and hydrophilic group is 0.005M.

18. The rinse liquid in which the hydrocarbon compound having hydrophobic group  
 and hydrophilic group is dissolved in deionized water. The chemical formula of the  
 hydrocarbon compound is  $C_aH_bO_cS_dN_eP_f$ , where a is an integer ranging from 1 to 30, b is an  
 integer ranging from 1 to 60, c is an integer ranging from 1 to 10, d is an integer ranging  
 25 from 0 to 2, e is an integer ranging from 0 to 2, f is an integer ranging from 0 to 2. If the  
 compound is alcohol, a is an integer ranging from 5 to 30, b is an integer ranging from 1 to  
 60, c is an integer ranging from 1 to 10, d is an integer ranging from 0 to 2, e is an integer  
 ranging from 0 to 2, f is an integer ranging from 0 to 2.

19. In claim 18, the rinse liquid is made by the hydrocarbon compound whose the hydrophobic group is saturated hydrocarbon or unsaturated hydrocarbon and the hydrophilic group is carboxylic acid, sulfonic acid or alcohol.

5 20. In claim 18, the rinse liquid is made by the following chemical.

dodecyl sulfuric acid  $C_{12}H_{25}SO_4H$ , dodecyl monooxyethylene sulfuric acid  $C_{12}H_{25}(OCH_2CH_2)SO_4H$ , dodecyl dioxyethylene sulfuric acid  $C_{12}H_{25}(OCH_2CH_2)_2SO_4H$ , dodecyl trioxyethylene sulfuric acid  $C_{12}H_{25}(OCH_2CH_2)_3SO_4H$ , dodecyl hexaoxyethylene sulfuric acid,  $C_{12}H_{25}(OCH_2CH_2)_6SO_4H$ .

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21. In claim 18 or claim 19 or claim 20,

The concentration of the hydrocarbon surfactant having hydrophobic group and hydrophilic group is ranging from 0.001M to 10M.

15 22. In claim 21,

The concentration of the hydrocarbon surfactant having hydrophobic group and hydrophilic group is 0.05M.

23. The rinse liquid is made by using the salt compound of the fluorocarbon surfactant  
20 having hydrophobic group and hydrophilic group with  $Li$ ,  $Na$ , or  $NH_aR^+_bOH^-$  where  $a$  is an integer ranging from 0 to 4,  $b$  is an integer ranging from 0 to 4,  $R$  is  $CH_3$ ,  $C_4H_9$ ,  $C_3H_7$ ,  $C_2H_4OH$ , or moiety having alkyl or alcohol or ether whose number of carbon is ranging from 1 to 20.

25 24. The rinse liquid is made by using the salt compound of the hydrocarbon compound having hydrophobic group and hydrophilic group with  $Li$ ,  $Na$ , or  $NH_aR^+_bOH^-$  where  $a$  is an integer ranging from 0 to 4,  $b$  is an integer ranging from 0 to 4,  $R$  is  $CH_3$ ,  $C_4H_9$ ,  $C_3H_7$ ,  $C_2H_4OH$ , or moiety having alkyl or alcohol or ether whose number of carbon is ranging from 1 to 20.

25. In claim 23 or claim 24, The rinse liquid is made by using the salt compound of the fluorocarbon or hydrocarbon compound having hydrophobic group and hydrophilic group with  $\text{NH}_4\text{R}^+\text{OH}^-$  which is one of following compound; ammoniumhydroxide, Tetramethyl ammoniumhydroxide, Tetrabutyl ammoniumhydroxide, Tetrapropyl ammoniumhydroxide, 5 ethanol ammoniumhydroxide, diethanol ammoniumhydroxide, triethanol ammoniumhydroxide.

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1/6

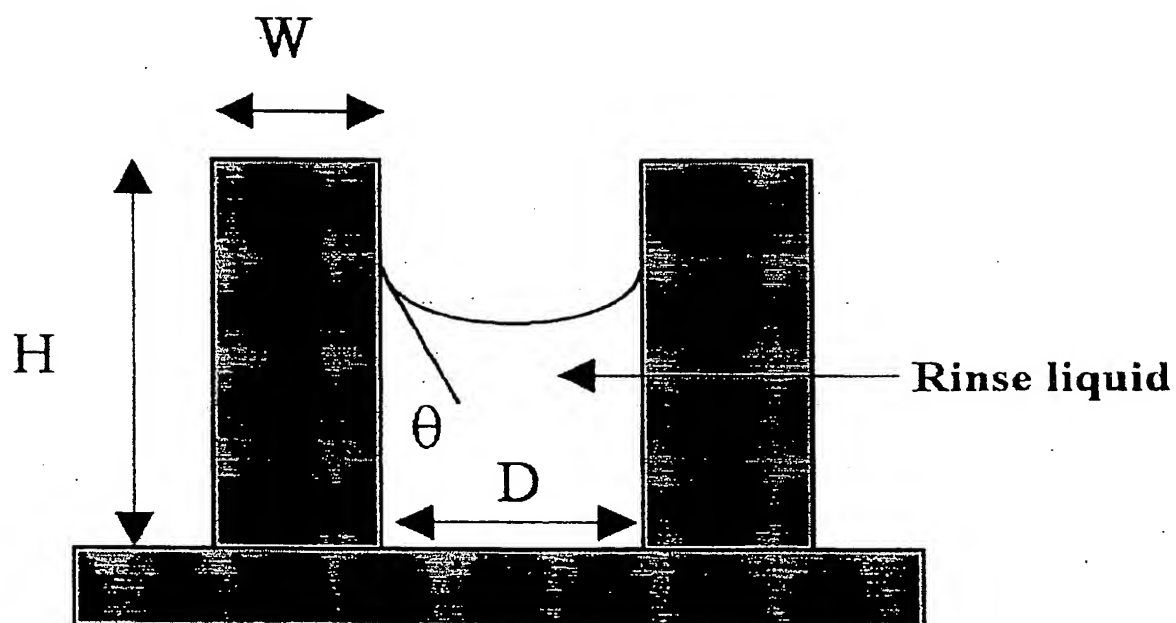


Fig. 1

2/6

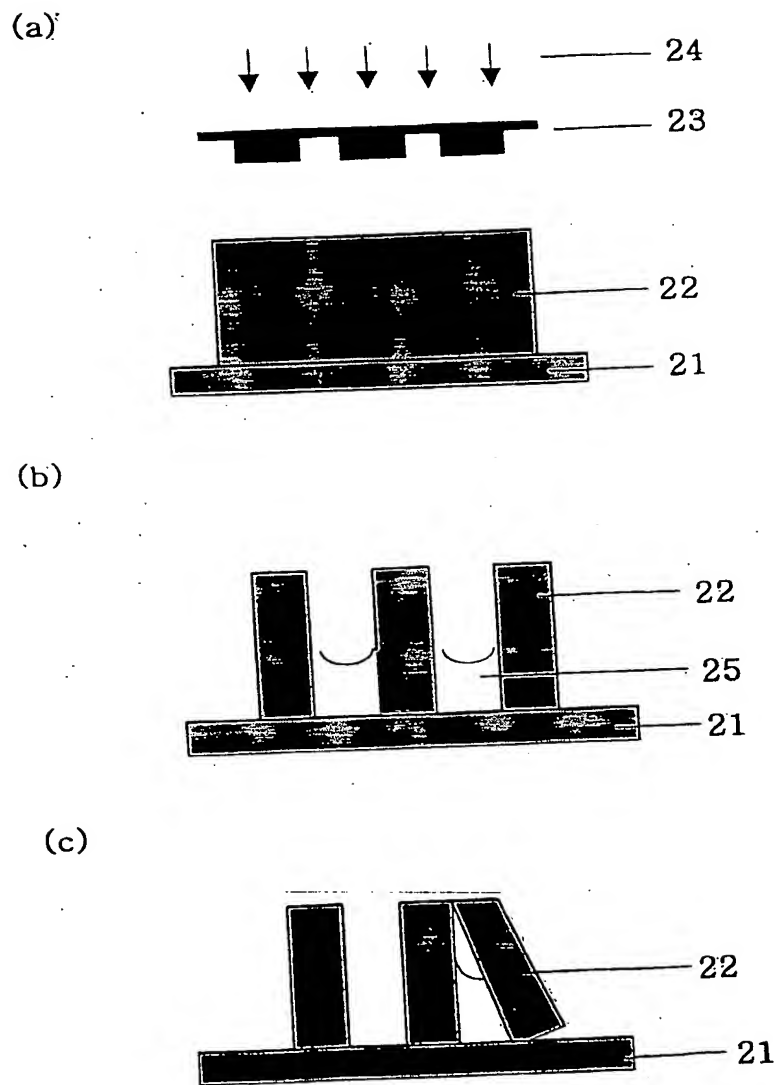


Fig. 2



3/6

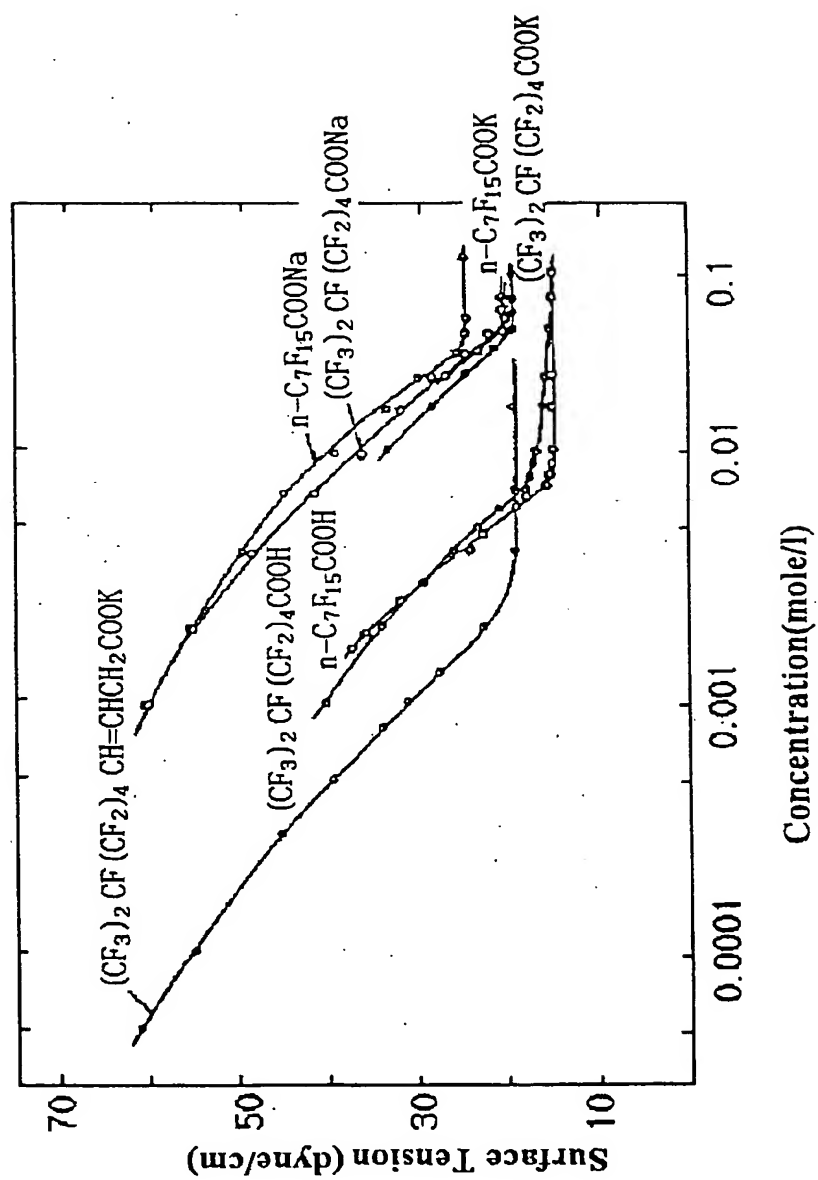
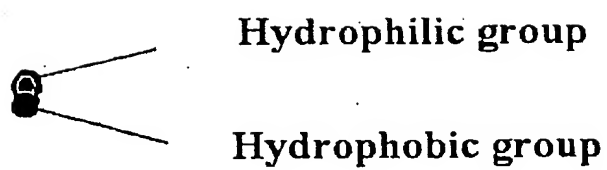
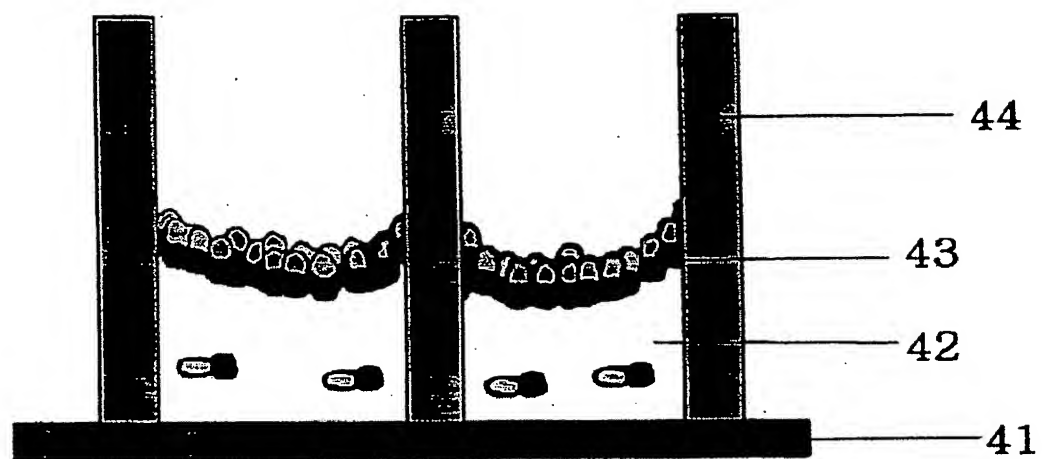


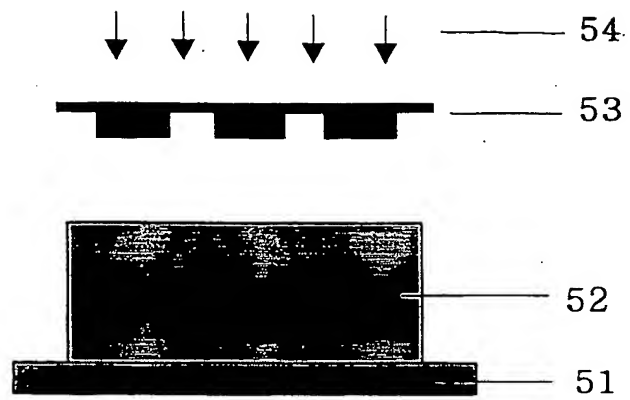
Fig. 3

4/6

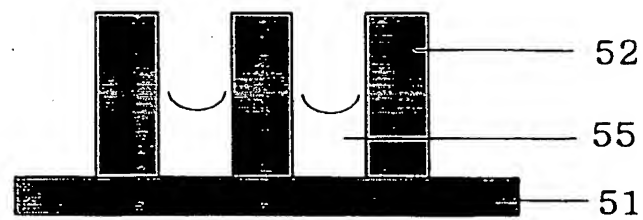
**Fig. 4**

5/6

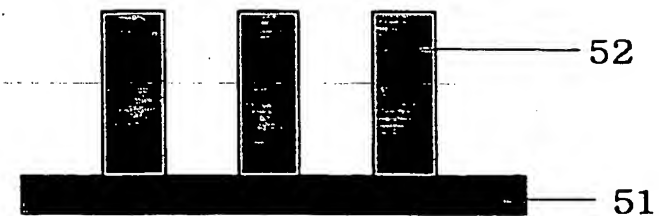
(a)



(b)



(c)

**Fig. 5**

6/6

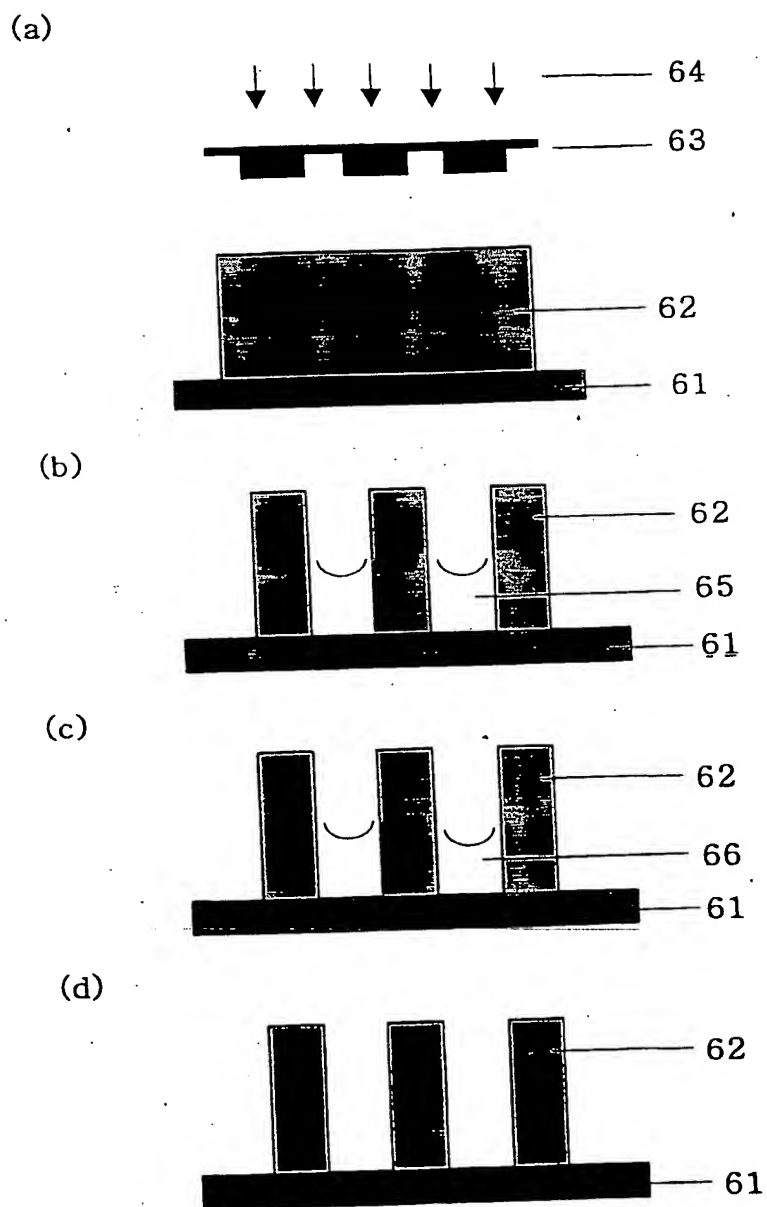


Fig. 6

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/KR02/00188

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC7 H01L 21/027, G03F 7/039, H01L 21/306

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

KR, JP : IPC7 H01L, G03F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

KOREAN PATENTS AND APPLICATIONS FOR INVENTIONA SINCE 1975

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

KIPONET

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                 | Relevant to claim No.            |
|-----------|--|----------------------------------|
| Y         | JP 9-82629 A (SOLTEC:KK, ESASHI MASAKI) 28 March 1997<br>see abstract; claims 1-5; fig.3-6<br>---- | 1-4, 6-11<br>13-14, 18-19, 23-24 |
| Y         | JP 12-258924 A (MITSUBISHI GAS CHEM. CORP. INC.) 22 Sep. 2000<br>see whole document<br>----        | 1-4, 6-11<br>13-14, 18-19, 23-24 |
| Y         | KR 98-171943 B (HYUNDAI ELECTRONIC CORP.) 3 March 1999<br>see abstract; fig.1<br>----              | 1-4, 6-11<br>13-14, 18-19, 23-24 |
| Y         | JP 11-67632 A (MITSUBISHI GAS CHEM. CORP. INC.) 9 March 1999<br>see whole document<br>----         | 13-14, 18-19, 23-24              |
| Y         | JP 10-27771 A (OMI TADAHIRO) 27. Jan. 1998<br>see whole document<br>----                           | 13-14, 18-19, 23-24              |
| A         | JP 12-138156 A (NIPPON TELEGR. & TELEPH. CORP.<NTT>) 16 May 2000<br>see abstract; fig.5-6<br>----  | 1-4, 6-11<br>13-14, 18-19, 23-24 |
| A         | JP 11-249323 A (KAO CORO.) 17 Sep. 1999<br>see the whole document<br>----                          | 1-4, 6-11<br>13-14, 18-19, 23-24 |

☒ Further documents are listed in the continuation of Box C.☐ See patent family annex.

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"&amp;" document member of the same patent family


Date of the actual completion of the international search

10 MAY 2002 (10.05.2002)

Date of mailing of the international search report

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LEE, Doo Han

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## INTERNATIONAL SEARCH REPORT

International application No.

PCT/KR02/00188

| C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT |  |                                  |
|---|--|----------------------------------|
| Category*   | Citation of document, with indication, where appropriate, of the relevant passages               | Relevant to claim No.            |
| A   | JP 8-8163 A (SONY CORO.) 12 Jan. 1996<br>see claims 1-8; fig.3-4<br>----                         | 1-4, 6-11<br>13-14, 18-19, 23-24 |
| A   | JP 7-20637 A (HITACHI LTD., SOLTEC:KK) 24 Jan. 1995<br>see claims 1-16; fig.1-3, 5<br>----       | 1-4, 6-11<br>13-14, 18-19, 23-24 |
| PY  | JP 13-100436 A (MITSUBISHI GAS CHEM. CORP. INC.) 16 April 2001<br>see the whole document<br>---- | 1-4, 6-11<br>13-14, 18-19, 23-24 |

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